

Supporting information for

**Enhancement of Polymer Structural Ordering
in Polymer-stabilized Blue Phases for Improved
Electro-Optical Properties**

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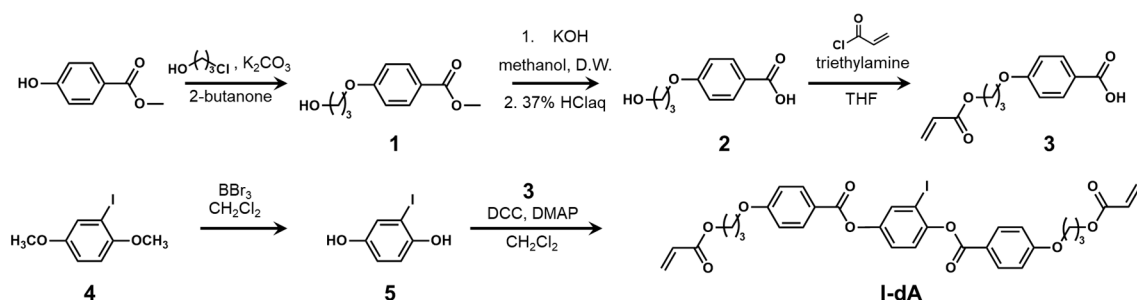
Materials

All reagents and solvents were purchased from commercial sources and used without further purification. **I-mA**¹, **I-mMA**¹ and **4**² were synthesized as reported procedures.

Measurements

¹H NMR and ¹³C NMR spectra were measured on a JEOL JNM-ECX400 apparatus at 400 MHz.

Scheme S1. Synthesis of **I-dA**.



Synthesis of **1**

To a solution of K_2CO_3 (36.3 g, 262.88 mmol) and methyl 4-hydroxybenzoate (10 g, 60.2 mmol) in 2-butanone (155 mL) was added slowly a solution of 1-chloro-3-propanol (6.21 g, 65.72 mmol) in 2-butanone (15 mL). After refluxing 48 h, distilled water (D.W.) was added and extracted with CH_2Cl_2 . The solution was dried over $MgSO_4$, followed by evaporation to afford 12.30 g (83%) of product **1**. ¹H NMR (400 MHz, $DMSO-d_6$, TMS standard, r.t.) δ = 7.90 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 8.9, 2H), 4.58 (t, J = 5.1 Hz, 1H), 4.11 (t, J = 6.3 Hz, 2H), 3.81 (s, 3H), 3.56 (q, J = 6.0, 2H), 1.88 (quin, J = 6.3 Hz, 2H).

Synthesis of **2**

A solution of **1** (12.00 g, 53.51 mmol) and KOH (4.50 g, 80.27 mmol) in D.W. (80 mL) and ethanol (113 mL) was refluxed for six hours. After cooling to r.t., to the reaction solution was acidified to pH 2 with 37% HCl aq. and extracted by EtOAc. The solvents were evaporated to afford 8.43 g (80%) of product **2**. ¹H NMR (400 MHz, $DMSO-d_6$, TMS standard, r.t.) δ = 12.64 (s, 1H), 7.88 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.61 (s, 1H), 4.11 (t, J = 6.4 Hz, 2H), 3.56 (s, 2H), 1.88 (quin, J = 6.25, 2H).

Synthesis of **3**

To a solution of triethylamine (11.2 mL, 80.38 mmol) and **2** (7.80 g, 39.76 mmol) in anhydrous THF (105 mL) was slowly added acryloyl chloride (4.83 mL, 59.63 mmol) under N_2 atmosphere in

the iced bath. The reaction solution was stirred at r.t. for 16 h and at 45 °C for 3 h, and the reaction solution was evaporation to dryness. The residue was solved with CH₂Cl₂ and the organic layer was washed with 5% HCl aq. and D.W., followed by drying over anhydrous Na₂SO₄. Solvents were evaporated and the residue was purified by flash silica gel column chromatography (EtOAc/heptane = 1/1) to afford 6.05 g (65%) of product **3**. ¹H NMR (400 MHz, CDCl₃, TMS standard, r.t.) δ = 8.05 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.42 (dd, *J* = 17.1 Hz, 1H), 6.13 (dd, *J* = 17.1 Hz, 1H), 5.84 (dd, *J* = 10.2 Hz, 1H), 4.38 (t, *J* = 6.3 Hz, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 2.20 (m, 2H).

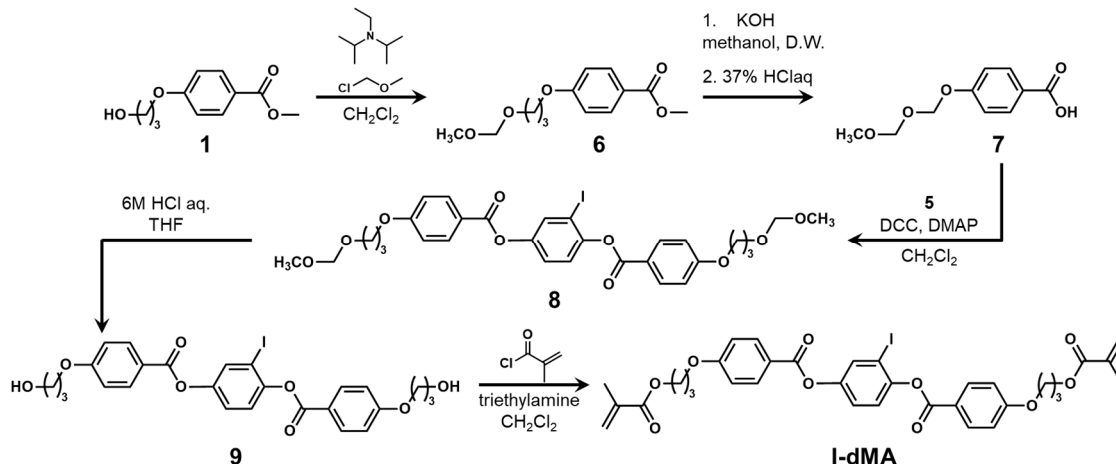
Synthesis of **5**

A solution of BBr₃ (25 g, 100.35 mmol) in CH₂Cl₂ (57 mL) was added to a solution of **4** in anhydrous CH₂Cl₂ at -78 °C. The solution was stirred at r.t. for 12 h and the reaction was worked up by adding iced water. The organic layer was washed with D.W. and dried over anhydrous MgSO₄. Solvents were evaporated and the residue was purified by silica gel column chromatography to afford 2.28 g (48%) of product **5**. ¹H NMR (400 MHz, CDCl₃, TMS standard, r.t.) δ = 7.16 (d, *J* = 2.9 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.76 (dd, *J* = 8.8, 2.9 Hz, 1H).

Synthesis of **I-dA**

To a solution of **5** (0.50 g, 2.12 mmol) and **3** (0.50 g, 2.12 mmol) in CH₂Cl₂ (70 mL) was added dicyclo hexyl carbodiimide (4.05 g, 19.63 mmol), 4-(dimethyl amino) pyridine (1.70 g, 13.92 mmol). The solution was stirred at r.t. for 24 h, and the solvents were evaporated to dryness after filtration. The residue was purified by silica gel column chromatography, followed by recrystallization from EtOAc/ethanol to afford 0.80 g (57%) of product **6**. ¹H NMR (400 MHz, DMSO-*d*₆, TMS standard, r.t.) δ = 8.16 (d, *J* = 8.9 Hz, 2H), 8.09 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.42 (m, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.36 (dd, *J* = 17.3 Hz, 1.5 Hz, 2H), 6.20 (dd, *J* = 17.3, 10.3 Hz, 2H), 5.96 (dd, *J* = 10.3, 1.5 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 4H), 4.29 (t, *J* = 6.4 Hz, 4H), 4.21 (m, 4H), 2.14 (q, *J* = 6.3 Hz, 2H), 2.13 (q, *J* = 6.2 Hz, 2H). ¹³C NMR (400 MHz, CDCl₃, TMS standard, r.t.) δ = 166.14, 164.43, 163.89, 163.34, 163.28, 149.00, 148.61, 132.67, 132.40, 132.32, 131.07, 128.45, 123.25, 122.78, 121.38, 121.32, 114.40, 114.36, 90.02, 64.66, 61.13, 28.48., HRMS (EI) Calcd for C₃₂H₂₉IO₁₀ [M]⁺: m/z 700.0805. Found: m/z 700.0806.

Scheme S2. Synthesis of I-dMA.



Synthesis of 6

To a solution of **1** (16.50 g, 78.5 mmol) and diisopropylethylamine (26.70 mL, 157 mmol) in CH_2Cl_2 in iced bath was slowly added chloro methyl ether (7.58 g, 94.2 mmol) and the solution was stirred at r.t. for 12 h. The organic layer was washed with D.W. and extracted by CH_2Cl_2 , followed by drying over MgSO_4 . After evaporating the solvent, the residue was purified by silica gel column chromatography to afford 16.23 g (81%) of product **6**. ^1H NMR (400 MHz, CDCl_3 , TMS standard, r.t.) δ = 7.98 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 4.63 (s, 2H), 4.13 (t, J = 5.8 Hz, 2H), 3.87 (s, 3H), 3.73 (t, J = 5.8 Hz, 2H), 3.34 (s, 3H), 2.09 (m, 2H).

Synthesis of 7

A mixture of **6** (16.27 g, 63.98 mmol) and KOH (5.39 g, 95.98 mmol) in D.W. and ethanol was refluxed for 6 h. The reaction mixture was cooled down to r.t. and was acidified to pH 2 with 37% HCl aq. After evaporating the solvents, the residue was purified by recrystallization from methanol to afford 12.95 g (80%) of product **7**. ^1H NMR (400 MHz, CDCl_3 , TMS standard, r.t.) δ = 8.05 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 9.7 Hz, 2H), 4.64 (s, 2H), 4.16 (t, J = 6.3 Hz, 2H), 3.73 (t, J = 5.8 Hz, 2H), 3.35 (s, 3H), 2.10 (m, 2H).

Synthesis of 8

To a solution of **5** (2.05 g, 86.9 mmol) and **7** (4.13 g, 17.06 mmol) in CH_2Cl_2 (25 mL) were added dicyclo hexyl carbodiimide (3.52 g, 170.6 mmol), 4-(dimethyl amino)pyridine (0.42 g, 34.3 mmol), and the mixture was stirred at r.t. for 24 h and filtered. The solvents were evaporated, and the residue was purified by silica gel column chromatography (EtOAc/toluene = 5/95), followed by recrystallization from EtOAc/EtOH to afford 4.35 g (75%) of product **8**. ^1H NMR (400 MHz, CDCl_3 , TMS standard, r.t.) δ = 8.22 (d, J = 8.7 Hz, 2H), 8.13 (d, J = 8.7 Hz, 2H), 7.73 (s, 1H), 7.28 (s, 2H),

7.00 (t, $J = 9.2$ Hz, 4H), 4.65 (s, 4H), 4.19 (t, $J = 5.8$ Hz, 4H), 3.74 (t, $J = 5.8$ Hz, 4H), 3.36 (s, 6H), 2.12 (m, 4H).

Synthesis of **9**

A mixture of **8** (4.30 g, 680.48 mmol), 6 M HCl aq. (100 mL) and THF (100 mL) was stirred at r.t. for 48 h. The mixture was extracted with CH₂Cl₂ and the solvents were evaporated, followed by recrystallization from EtOAc to afford 2.27 g (61%) of product **9**. ¹H NMR (400 MHz, CDCl₃, TMS standard, r.t.) δ = 8.22 (d, $J = 8.8$ Hz, 2H), 8.13 (d, $J = 8.8$ Hz, 2H), 7.74 (s, 1H), 7.54 (d, $J = 8.8$, 1H), 7.01 (d,d, $J = 8.8$, 9.8 Hz, 4H), 6.90 (d, $J = 8.8$, 1H), 4.23 (t, $J = 5.8$ Hz, 2H), 4.22 (t, $J = 6.2$, 2H), 3.90 (t, $J = 5.8$ Hz, 4H), 2.10 (quin, $J = 5.8$, 4H).

Synthesis of **I-dMA**

To a solution of triethylamine (1.89 mL, 13.5 mmol) and **9** (2.00 g, 3.38 mmol) in anhydrous CH₂Cl₂ (25 mL) under N₂ atmosphere in iced bath was slowly added methacryloyl chloride (0.95 mL, 10.1 mmol) and stirred over night at r.t. The reaction mixture was extracted with CH₂Cl₂ and dried over anhydrous Na₂SO₄. The solvents were evaporated, and the residue was purified by silica gel column chromatography (EtOAc/CH₂Cl₂ = 5/95) to afford 1.90 g (77%) of product **I-dMA**. ¹H NMR (400 MHz, DMSO-*d*₆, TMS standard, r.t.) δ = 8.14 (d, $J = 8.7$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 1.9$, 1H), 7.43 (m, 2H), 7.17 (d, $J = 9.0$, 2H), 7.14 (d, $J = 9.0$, 2H), 6.06 (s, 2H), 5.70 (s, 2H), 4.29 (t, $J = 6.0$ Hz, 4H), 4.22 (t,t, $J = 5.5$ Hz, 4H), 2.14 (m, 4H), 1.96 (s, 6H). ¹³C NMR (400 MHz, CDCl₃, TMS standard, r.t.) δ = 167.35, 164.44, 163.90, 163.36, 163.30, 149.01, 146.61, 136.21, 132.68, 132.42, 132.33, 125.71, 123.25, 122.79, 121.37, 121.31, 114.39, 114.36, 90.03, 64.76, 61.29, 28.51, 18.35. HRMS (EI) Calcd for C₃₄H₃₃IO₁₀ [M]⁺: m/z 728.1118. Found: m/z 728.1117.

References

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2. Pavlinak, J.; Zupan, M.; Stavber, S. Effect of Water on the Functionalization of Substituted Anisoles with Iodine in the Presence of F-TEDA-BF₄ or Hydrogen Peroxide. *J. Org. Chem.* **2006**, *71*, 1027–1032, doi:10.1021/jo05202.